Ketonisation of carboxylic acids over Zn-Cr oxide in the gas phase

Hossein Bayahia, Elena F. Kozhevnikova, Ivan V. Kozhevnikov*

Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, United Kingdom

ABSTRACT

Bulk Zn(II)-Cr(III) mixed oxides with a Zn/Cr atomic ratio of 1:1–20:1 were found to be active catalysts for the gas-phase ketonisation of carboxylic acids (acetic and propionic) to form acetone and 3-pentanone, respectively, at 300–400 °C and ambient pressure. Zn-Cr (10:1) oxide showed the best performance, significantly exceeding that of the parent oxides ZnO and Cr_2O_3. The catalytic activity was further enhanced by supporting Zn-Cr (10:1) oxide on TiO_2 and γ-Al_2O_3. With 20%Zn-Cr/Al_2O_3, ketonisation of propionic acid occurred with 97% selectivity to 3-pentanone at 99% conversion at 380 °C. Zn-Cr oxides were characterised by BET, XRD, DRIFTS of pyridine and acetic acid adsorption and microcalorimetry of ammonia adsorption. From DRIFTS, carboxylic acid adsorbed dissociatively on Zn-Cr oxide to form a surface metal carboxylate in bidentate bridging bonding mode. A mechanism for ketonisation of carboxylic acids via β-ketoacid intermediate route has been proposed.

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1. Introduction

Carboxylic acids, readily available from natural resources, are attractive as renewable raw materials for the production of value-added chemicals and bio-fuels [1,2]. For fuel applications, carboxylic acids require reduction in their oxygen content to increase their caloric value. Therefore, much current research is focussed on deoxygenation of carboxylic acids using heterogeneous catalysis [3–7].

Ketonisation of carboxylic acids, also known as ketonic decarboxylation, is a reaction which converts two carboxylic acid molecules into a ketone, carbon dioxide and water (Eq. (1)). It is widely employed as a clean, non-polluting method for the synthesis of ketones [8,9]. Once found its industrial application for the production of acetone, this reaction is regaining interest for the upgrading of biomass-derived oxygenates, for example, bio-oil obtained from fast pyrolysis of biomass. Bio-oil, amongst other oxygenate molecules such as furanics and phenolics, contain lower carboxylic acids, which can be upgraded to obtain gasoline, diesel or platform chemicals [1,2,9]. Ketonisation is crucial to reduce the adverse effects of carboxylic acids in bio-oil, as it can remove the highly reactive carboxylic groups while increasing the length of the carbon chain to yield a more stable ketone product with higher caloric value. The ketones produced can be further upgraded by aldol condensation to increase the product fraction that falls in the gasoline/diesel range.

Ketonisation of carboxylic acids in the gas phase is catalysed by many oxides and mixed oxides, as well as zeolites and heteropoly acids in the temperature range of 250–500 °C [8–17]. But the nature of catalytically active sites and reaction mechanism are not yet clear despite numerous research efforts during the past three decades [8,9]. In continuous search for better ketonisation catalysts with low cost and high activity, there are specific challenges which include the improvement of catalyst stability to minimise deactivation of ketonisation catalysts [9].

$$2RCOOH \rightarrow R_2CO + CO_2 + H_2O \qquad (1)$$
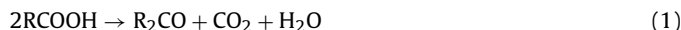
We now report that Zn(II)-Cr(III) mixed oxides prepared by co-precipitation of Zn(II) and Cr(III) hydroxides are active and durable catalysts for the ketonisation of carboxylic acids (acetic and propionic) in the gas phase to yield acetone and 3-pentanone, respectively, which are widely used as solvents and starting reagents for organic synthesis. Previously, Zn-Cr oxides have been used as catalysts for various reactions such as synthesis of methanol from the synthesis gas [18], fluorination of hydrocarbons, dehydrogenation of alcohols, hydrogenation of carboxylic acids and dehydroisomerisation of alpha-pinene to para-cymene ([19,20] and references therein). Pd/Zn-Cr has been reported as a bifunctional catalyst for the synthesis of methyl isobutyl ketone [20]. To our knowledge, Zn-Cr oxides have not been reported as the catalysts for acid ketonisation so far.

2. Experimental

2.1. Catalysts preparation

All chemicals were purchased from Sigma-Aldrich and used as supplied without further purification. Acetic and propionic acids were ≥99.5% pure. Cr(III) oxide, Zn(II) oxide and a series of Zn–Cr mixed oxides with various Zn/Cr atomic ratios were prepared by (co)-precipitation of Zn(II) and Cr(III) hydroxides [19,20]. This was carried out by adding dropwise 10 wt% aqueous ammonia to a stirred aqueous solution of a mixture of Zn(II) and Cr(III) nitrates ($[Zn^{+2}] + [Cr^{+3}] = 0.2$ M) at 70 °C until pH 7.0 was achieved, followed by aging the slurry for 3 h at 70 °C. The precipitates were filtered off, washed with distilled water until ammonia-free, dried in air at 110 °C overnight and finally calcined under nitrogen flow for 5 h at 300 °C. The oxides were ground into a powder with a particle size of 45–180 μm. Supported catalysts comprising 20 wt% Zn-Cr (10:1) on SiO$_2$, TiO$_2$ and γ-Al$_2$O$_3$ were prepared by co-impregnation of Zn(II) and Cr(III) nitrates onto support (Aerosil 300, Titanoxid P25 and Aluminiumoxid C from Degussa) from aqueous solution, followed by rotary evaporation of water, oven drying at 110 °C overnight and air calcination at 400 °C for 2 h to decompose the nitrates to oxides [21].

2.2. Catalyst characterisation

The specific surface area and porosity of catalysts were determined by the BET method from nitrogen physisorption measured at −196 °C on a Micromeritics ASAP 2010 instrument. Before analysis, the samples were evacuated in situ at 250 °C for 3 h. Powder X-ray diffraction (XRD) of catalysts was measured on a PANalytical Xpert diffractometer using a monochromatic CuKα radiation (λ = 1.542 Å) in a 2θ range of 20–80°. DRIFTS (diffuse reflectance infrared Fourier transform spectra) of adsorbed pyridine were taken on a Nicolet Nexus FTIR spectrometer as described elsewhere [22]. Catalyst samples were ground with KBr (10 wt% in KBr) and pre-treated at 150 °C/10^{-5} bar for 1 h. The samples were then exposed to pyridine vapour at room temperature for 1 h, followed by pumping out at 150 °C/10^{-5} bar for 1 h to remove physisorbed pyridine. Then the DRIFT spectra of adsorbed pyridine were recorded at room temperature at a resolution of 4 cm^{-1}. The same instrument was used to record DRIFT spectra of acetic acid adsorbed on bulk Zn-Cr oxide. Acetic acid was adsorbed at room temperature followed by evacuation at 160 °C/10^{-5} bar for 1 h to remove physisorbed acid. The DRIFT spectra were recorded at room temperature (4 cm^{-1} resolution). Differential heats of ammonia adsorption on the catalysts were measured at 150 °C by a pulse method in a flow system using a Setaram TG-DSC 111 differential scanning calorimeter as described previously [22].

2.3. Catalyst testing

The gas-phase ketonisation of carboxylic acids was carried in flowing N$_2$ at 300–400 °C under atmospheric pressure in a downflow quartz fixed-bed reactor (9 mm i.d.) with online GC analysis (Varian 3800 instrument with a 30 m × 0.32 mm × 0.5 μm Zebron ZB-WAX capillary column and a flame ionisation detector). For more accurate analysis of C$_1$–C$_3$ hydrocarbon products, a 60 m × 0.32 mm GS-GasPro capillary column was used, which allowed for full separation of these hydrocarbons. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. Carboxylic acid was fed by passing the carrier gas flow controlled by a Brooks mass flow controller through a stainless steel saturator which held the liquid acid at appropriate temperature to maintain the chosen reactant concentration in the gas flow. The downstream gas lines

Table 1
Catalyst characterisation.

Catalyst[a]	S_{BET}[b] (m^2 g^{-1})	Pore volume[c] (cm^3 g^{-1})	Pore size[d] (Å)
Cr$_2$O$_3$	243	0.26	42
Zn-Cr (1:6)	230	0.32	55
Zn-Cr (1:1)	136	0.11	32
Zn-Cr (3:1)	101	0.10	56
Zn-Cr (10:1)	43	0.10	90
Zn-Cr (20:1)	13	0.03	87
Zn-Cr (30:1)	10	0.02	86
ZnO	12	0.03	98
20% Zn-Cr(10:1)/SiO$_2$	156	0.60	153
20% Zn-Cr(10:1)/Al$_2$O$_3$	81	0.39	195
20% Zn-Cr(10:1)/TiO$_2$	45	0.11	102

[a] Bulk oxides calcined at 300 °C under N$_2$ for 5 h, supported catalysts calcined at 400 °C under air for 2 h.
[b] BET surface area.
[c] Single point total pore volume.
[d] Average BET pore diameter.

and valves were heated to 180 °C to prevent substrate and product condensation. The reactor was packed with 0.2 g catalyst powder of 45–180 μm particle size. Typically, the reaction was carried out at a carboxylic acid concentration of 2 vol% and an N$_2$ flow rate of 20 mL min^{-1} (space time $W/F = 4.0$ h g mol^{-1}, where W is the catalyst weight (g) and F the total molar flow rate (mol h^{-1})). Prior to reaction, the catalysts were heated at the reaction temperature in N$_2$ flow for 1 h. Once reaction started, the downstream gas flow was analysed by the on-line GC to obtain reactant conversion and product selectivity. The selectivity was defined as the percentage of carboxylic acid converted into a particular product taking into account the reaction stoichiometry; thus, 100% ketone selectivity would mean 1 mol of carboxylic acid converted to form 0.5 mol of the ketone. CO and CO$_2$ were not quantified and not included in reaction selectivities. The mean absolute percentage error in conversion and selectivity was ≤10% and the carbon balance was maintained within 95%..

3. Results and discussion

3.1. Catalyst characterisation

The texture (surface area, pore volume and pore diameter) of the catalysts studied is given in Table 1. The surface area and the pore volume of Zn-Cr mixed oxides increased significantly with increasing the Cr content from 12 m^2 g^{-1} at zero Cr content to 243 m^2 g^{-1} at 100% Cr content. The Zn-Cr (10:1) mixed oxide that showed the best catalytic performance in ketonisation (see below) had a surface area of 43 m^2 g^{-1}, a pore volume of 0.10 cm^3 g^{-1} and an average pore diameter of 90 Å. Zn-Cr (10:1) oxide exhibited an adsorption isotherm with an H3 hysteresis loop (Fig. 1) and a mononodal pore size distribution peaked at a 94 Å pore diameter (Fig. 2).

It has been reported that Zn–Cr oxides can be amorphous or crystalline depending on the calcination temperature and Zn/Cr atomic ratio [20]. Zn-rich oxides are crystalline materials, exhibiting ZnO phase. The oxides calcined at >350 °C also exhibit Cr$_2$O$_3$ and ZnCr$_2$O$_4$ spinel crystalline phases, the relative amounts of which depend on the Zn/Cr atomic ratio. From the XRD analysis (Fig. 3), ZnO exhibited the wurtzite phase (JCPDS file No. 36-1451). Zn-Cr (10:1) oxide calcined at 330 °C also exhibited wurtzite pattern, with the same crystallite size. This indicates that Zn^{2+} ions had similar location in both ZnO and Zn-Cr (10:1) oxide. Zn–Cr (1:6) oxide calcined at 300 °C was amorphous, but after calcination at 400 °C it exhibited the pattern of Cr$_2$O$_3$ phase, with a little of ZnCr$_2$O$_4$ spinel also present (Fig. 4).
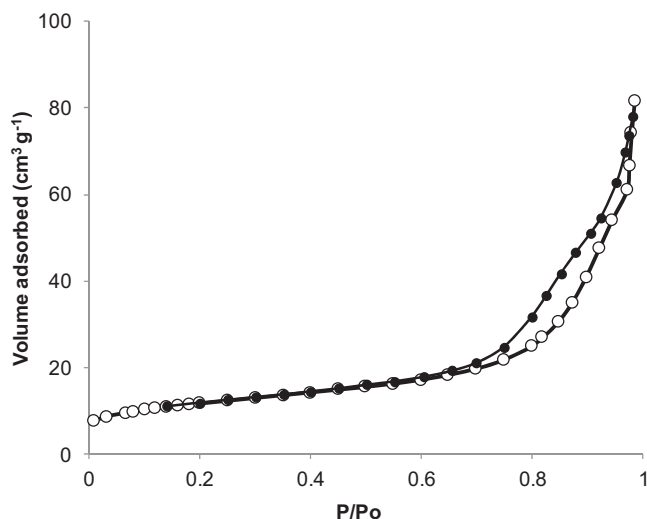
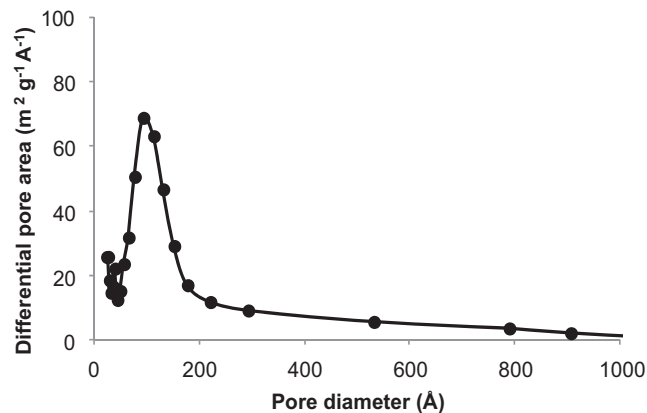**Fig. 1.** N_2 adsorption isotherm for Zn-Cr (10:1) oxide.

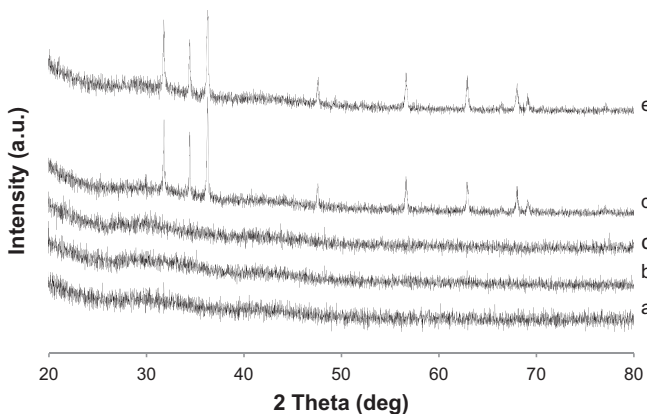**Fig. 2.** Pore size distribution for Zn-Cr (10:1) oxide.

Fig. 3. XRD for Zn-Cr oxide catalysts calcined at 330 °C under N_2 for 5 h (a) Cr_2O_3, (b) Zn-Cr (1:6), (c) Zn-Cr (1:1), (d) Zn-Cr (10:1), (e) ZnO.

Fig. 4. XRD for Zn-Cr (1:6) calcined at 400 °C under N_2 for 5 h.
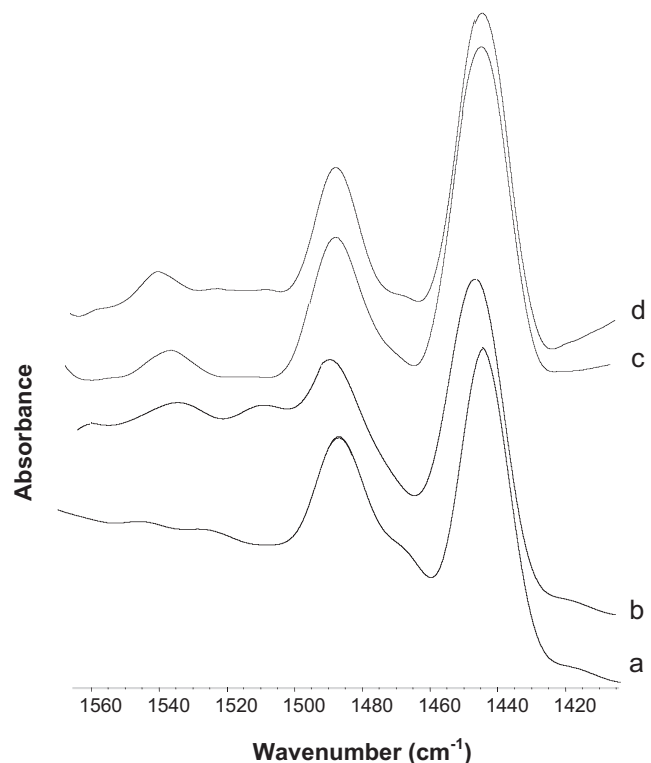
Fig. 5. DRIFT spectra of adsorbed pyridine: (a) ZnO, (b) Zn-Cr (10:1), (c) Zn-Cr (1:6), (d) Cr_2O_3.

The nature of acid sites and their relative amounts in Zn-Cr oxide catalysts was determined by the DRIFT spectroscopy of adsorbed pyridine from the characteristic infrared bands at 1540 (Brønsted acid sites) and 1440–1450 cm^{-1} (Lewis acid sites) [23]. In addition, a band at about 1490 cm^{-1} was observed (Fig. 5) which is attributed to pyridine adsorbed on both Brønsted and Lewis acid sites as well as H-bonded pyridine [23]. Since the bands at 1540 and 1440–1450 cm$^{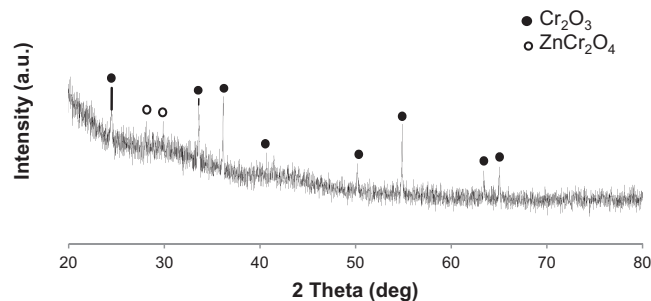-1}$ have approximately equal extinction coefficients [23], the ratio of their integral intensities gives directly the ratio of Brønsted and Lewis acid site densities (B/L). Zn–Cr (10:1) mixed oxide as well as its parent ZnO and Cr_2O_3 oxides predominantly had Lewis acid sites, as evidenced from the strong adsorption band at 1440–1450 cm^{-1} in their spectra (Fig. 5). Zn–Cr (10:1) and Cr_2O_3 had also a small number of Brønsted acid sites as indicated by the band at 1540 cm^{-1}, with a ratio of Brønsted and Lewis acid site densities B/L = 0.07. ZnO, however, did not show any Brønsted acid sites of sufficient strength to protonate pyridine.

The acid strength of catalysts was measured by ammonia adsorption microcalorimetry in terms of the differential enthalpy of ammonia adsorption at zero coverage (ΔH). This technique does not discriminate Brønsted and Lewis acidity, providing a measure of the total catalyst acid strength. The results are shown in Table 2. The acid strength of Zn-Cr oxides increased significantly with increasing the Cr content, with the ΔH values varying from −127 to −193 kJ mol^{-1}, which mostly represent the strength of Lewis acid sites in Zn-Cr oxides. The Zn-Cr (10:1) oxide had an intermediate acid strength of ΔH = −150 kJ mol^{-1}.

Table 2
Acidity of Zn-Cr oxide catalysts.

Catalyst[a]	Acid site type[b]	B/L[c]	ΔH[d] (kJ mol^{-1})
Cr$_2$O$_3$	B + L	0.07	−193
Zn-Cr (10:1)	B + L	0.07	−150
ZnO	L	0	−127

[a] Catalysts calcined at 300 °C in N$_2$ for 5 h.
[b] Brønsted (B) and Lewis (L) acid sites from DRIFTS of adsorbed pyridine.
[c] The ratio of intensities of the DRIFTS peaks at 1540 cm^{-1} and 1450 cm^{-1}.
[d] Differential enthalpy of NH$_3$ adsorption at 100 °C (±3 kJ mol^{-1}) [20].

Table 3
Ketonisation of aceic acid over bulk Zn-Cr oxide catalysts.[a]

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)	
			Acetone	Others[b]
ZnO	350	4	100	0
Zn-Cr (30:1)	350	11	100	0
Zn-Cr (20:1)	350	33	100	0
Zn-Cr (10:1)	300	16	100	0
Zn-Cr (10:1)	350	86	100	0
Zn-Cr (10:1)	380	99	95	4
Zn-Cr (10:1)	400	100	93	6
Zn-Cr (3:1)	350	69	99	1
Zn-Cr (1:1)	350	50	99	1
Cr$_2$O$_3$	350	10	100	0

[a] 1 bar pressure, 0.2 g catalyst, 20 mL min^{-1} N$_2$ flow rate, 2 vol% acetic acid, 4 h time on stream.
[b] Other products: methane, ethane and ethene; CO and CO$_2$ not included.

Table 4
Ketonisation of propionic acid over bulk Zn-Cr oxide catalysts.[a]

| Catalyst	Temperature	Conversion	Selectivity (%)	
	(°C)	(%)	3-Pentanone	Others[b]
None	330	0	0	0
ZnO	330	5	100	0
Zn-Cr (30:1)	330	21	100	0
Zn-Cr (20:1)	330	31	96	4
Zn-Cr (10:1)	330	45	98	2
Zn-Cr (10:1)	350	70	100	0
Zn-Cr (10:1)	380	98	94	7
Zn-Cr (10:1)	400	97	88	12
Zn-Cr (1:1)	330	48	81	9
Zn-Cr (1:6)	330	6	89	11
Cr$_2$O$_3$	330	3	100	0

[a] 1 bar pressure, 0.2 g catalyst, 20 mL min^{-1} N$_2$ flow rate, 2 vol% propionic acid, 4 h time on stream.
[b] Other products: C$_1$-C$_3$ alkanes and alkenes, 2-propanol; CO and CO$_2$ not included.

3.2. Catalyst performance

3.2.1. Bulk Zn-Cr oxides

Representative results obtained for the gas-phase ketonisation of acetic acid to acetone over the bulk Zn-Cr oxides in the temperature range of 300–400 °C are shown in Table 3. It can be seen that catalyst performance depended crucially on the Zn/Cr atomic ratio. Most interestingly, Zn-Cr mixed oxides showed significantly higher catalytic activities than either of the pure parent ZnO and Cr$_2$O$_3$ oxides, with Zn-Cr (10:1) oxide being the most active one. The catalyst activity increased with increasing the reaction temperature from 300 to 380 °C. At the optimum temperature of 380 °C, the Zn-Cr (10:1) oxide gave 95% selectivity to acetone at 99% acetic acid conversion (94% yield). Methane, ethane and ethene were formed as by-products, in addition to CO and CO$_2$ which were not monitored.

Similar results were obtained for propionic acid ketonisation giving 3-pentanone (Table 4). Again, Zn-Cr (10:1) mixed oxide showed the best performance at 380 °C to give 94% selectivity to
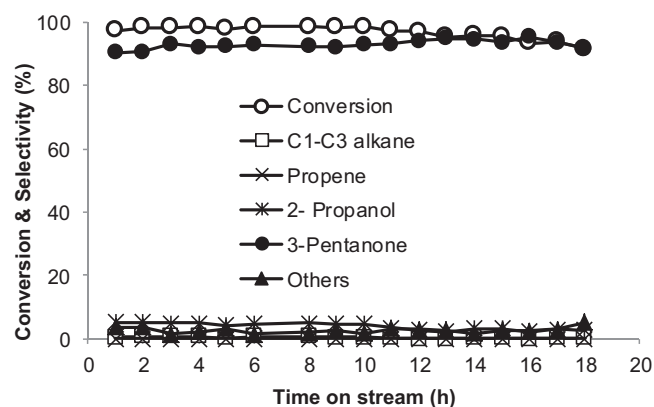
Fig. 6. Propionic acid conversion and product selectivity over bulk Zn:Cr (10:1) vs. time on stream (0.2 g catalyst, 380 °C, 1 bar pressure, 20 mL min^{-1} N$_2$ flow rate, 2 vol% propionic acid).

3-pentanone at 98% propionic acid conversion (92% yield). C$_1$–C$_3$ alkanes and alkenes and 2-propanol formed as by-products probably by decarbonylation and decarboxylation of propionic acid and acid-catalysed cracking of 3-pentanone. Fig. 6 shows the performance of Zn-Cr (10:1) oxide for 18 h time on stream; only a small drift in conversion from 98 to 95% at 3-pentanone selectivity of 93–95% can be seen over the time on stream. The catalyst exhibited stable performance in the reaction at 350 °C at a 70% conversion and 100% 3-pentanone selectivity without any deactivation for at least 6 h on stream (Supplementary Information, Fig. S1).

For Zn-Cr (10:1) oxide, the apparent activation energy was found to be 124 kJ mol^{-1} in the temperature range 300–320 °C (under differential conditions at a propionic acid conversion ≤10%), which indicates that the reaction occurred under kinetic regime in this temperature range and probably above up to 380 °C. This is also supported by the Weisz-Prater analysis [24] of the reaction system: Weisz-Prater criterion $C_{WP} = 1.2 \times 10^{-2} < 1$ indicating no internal diffusion limitations).

3.2.2. Supported Zn-Cr (10:1) oxide

Supporting Zn-Cr (10:1) oxide on γ-Al$_2$O$_3$ and TiO$_2$ was found to further improve the catalyst performance in propionic acid ketonisation as per the amount of Zn-Cr oxide in the catalyst (Table 5). These supports possessing considerable Brønsted and Lewis acidity were themselves found active in this reaction and hence contributed to the catalyst activity observed. In contrast, SiO$_2$, which is a rather neutral support, was inactive below 400 °C (Table 5), although it has been found active at higher temperatures [16]. Probably for this reason the silica-supported Zn-Cr (10:1) oxide exhibited only a moderate ketonisation activity at our reaction conditions. Best results were obtained with 20%Zn-Cr(10:1)/Al$_2$O$_3$ at 380 °C: 97% 3-pentanone selectivity at 99% propionic acid conversion (96% yield). This performance is considerably better than that obtained for the 20:80 w/w physical mixture of Zn-Cr (10:1) and Al$_2$O$_3$. The latter showed a conversion of 63%, close to the weighted sum of activities of Zn-Cr (10:1) and Al$_2$O$_3$ (Table 5). The enhanced catalytic activity of supported catalyst may be attributed to a higher dispersion of Zn-Cr oxide on the alumina surface. This is supported by our powder XRD data (Supplementary Information, Fig. S2 and S3). Bulk Zn-Cr(10:1) oxide and 20%Zn-Cr(10:1)/Al$_2$O$_3$ calcined at 380 °C/5 h were found to have a ZnO particle size of 52 ± 6 and 37 ± 1 nm, respectively, which indicates a higher dispersion of the ZnO phase in the supported catalyst compared to the bulk one.

Fig. 7 shows stable performance of 20%Zn-Cr(10:1)/Al$_2$O$_3$ catalyst for 24 h time on stream, with conversion only slightly drifting from 99 to 97% at a constant 3-pentanone selectivity of 94-95%. This small drift in conversion may be caused by catalyst coking: a

Table 5
Ketonisation of propionic acid over supported Zn-Cr (10:1) oxide catalysts.[a]

| Catalyst[a]	Temperature (°C)	Conversion (%)	Seletivity (%)	
			3-Pentanone	Others[b]
SiO$_2$	380	0	0	0
Al$_2$O$_3$	380	61	98	2
TiO$_2$	380	99	60	40
20% Zn-Cr(10:1)/SiO$_2$	350	12	100	0
20% Zn-Cr(10:1)/SiO$_2$	380	51	94	6
20% Zn-Cr(10:1)/SiO$_2$	400	56	90	10
20% Zn-Cr(10:1)/Al$_2$O$_3$	350	48	100	0
20% Zn-Cr(10:1)/Al$_2$O$_3$	380	99	97	3
Zn-Cr (10:1) + Al$_2$O$_3$ (20:80)[c]	380	63	97	3
20% Zn-Cr(10:1)/Al$_2$O$_3$	400	99	90	10
20% Zn-Cr(10:1)/TiO$_2$	350	65	97	3
20% Zn-Cr(10:1)/TiO$_2$	380	97	94	6
20% Zn-Cr(10:1)/TiO$_2$	400	100	88	12

[a] 1 bar pressure, 0.2 g catalyst, 20 mL min^{-1} N$_2$ flow rate, 2 vol% propionic acid, 4 h time on stream.
[b] Other products: C$_1$–C$_3$ alkanes and alkenes, 2-propanol; CO and CO$_2$ not included.
[c] Zn-Cr (10:1) + Al$_2$O$_3$ (20:80 w/w physical mixture).
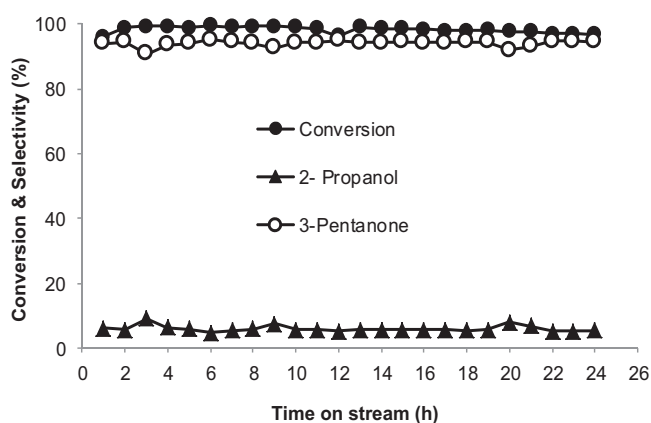
Fig. 7. Propionic acid conversion and product selectivity over 20% Zn-Cr(10:1)/Al$_2$O$_3$ vs. time on stream (0.2 g catalyst, 380 °C, 1 bar pressure, 20 mL min^{-1} N$_2$ flow rate, 2 vol% propionic acid).

small amount of coke was indeed found in the catalyst after this run (1.4% carbon content). The catalyst exhibited no any deactivation in the reaction at 350 °C at a 50% conversion and 100% 3-pentanone selectivity for at least 6 h on stream (Supplementary Information, Fig. S1).

It is generally difficult to compare the activity of catalysts reported by different groups due to different reaction conditions applied. Nevertheless, by the yield of 3-pentanone obtained, Zn-Cr (10:1) oxide is on a par with the best ketonisation catalysts reported so far [8,9], e.g., CeO$_2$-Mn$_2$O$_3$ [11]. The CeO$_2$-Mn$_2$O$_3$ oxide has a higher catalytic activity than either of the parent CeO$_2$ and Mn$_2$O$_3$ oxides, with the highest activity at a Ce/Mn atomic ratio of 2:3 providing an average 3-pentanone yield of 84–90% over 5 h time on stream at 350–400 °C and $W/F = 10$ h g mol^{-1} for propionic acid [11]. The activity of CeO$_2$ and MnO$_2$ in ketonisation of acetic and propionic acids has been found to increase upon their loading (20%) on Al$_2$O$_3$ [12], similar to Zn-Cr oxide.

3.2.3. Ketonisation mechanism

Ketonisation occurs with carboxylic acids possessing α-hydrogen atoms at least in one of the reacting acid molecules [8,9]. Several mechanisms have been proposed for this reaction [8,9]. These include: (i) decomposition of metal carboxylate, (ii) via acid anhydride intermediate, (iii) via β-ketoacid intermediate and (iv) via ketene intermediate route (for a recent review, see [9]). It is thought that basic and amphoteric materials are favourable
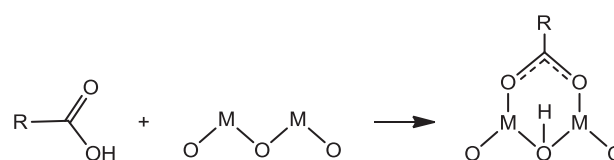

Scheme 1. Dissociative adsorption of carboxylic acid on a metal oxide.

catalysts for ketonisation [8,9]. However, heteropoly acid H$_3$PW$_{12}$O$_{40}$ possessing very strong proton sites and practically no bacisity has also been found active in propionic acid ketonisation at 200–250 °C, probably occurring via the ketene intermediate route [17]. This suggests that the mechanism may depend on many factors, especially the type of catalyst used.

Numerous IR spectroscopic studies have dealt with carboxylic acid adsorption on metal oxides, e.g., TiO$_2$, Al$_2$O$_3$, CeO$_2$, SnO$_2$, and MgO [25–29]. There is compelling evidence that carboxylic acids adsorb dissociatively on a pair of the neighbouring Lewis acid and base sites on the metal oxide surface to form a metal carboxylate in monodentate, bidentate chelate or bidentate bridging bonding mode. DFT analysis [29] shows that for adsorption of formic, acetic and propionic acids on metal oxides the bridging mode is more likely (Scheme 1), and such surface species have been suggested as possible intermediates for ketonisation of carboxylic acids [28,30].

Fig. 8 shows the DRIFT spectrum of acetic acid adsorbed on Zn-Cr (10:1) oxide measured in the absence of acetic acid in the gas phase after evacuation at 160 °C. This spectrum is similar to those reported previously for other metal oxides [25–29]. The absence of a peak characteristic of the C=O stretch in the region of 1690–1790 cm^{-1} clearly shows that there is no physisorbed acetic acid present. The peaks at 1424 and 1351 cm^{-1} can be assigned to C–H deformations. The bands at 1553 and 1462 cm^{-1} can be attributed to the antisymmetric and symmetric vibrations of the OCO group of acetate [25–29], which indicates the bridging mode for acetate bonding (Scheme 1) [29].

It is conceivable that over Zn-Cr oxides ketonisation occurs via the β-ketoacid intermediate route (Scheme 2), which is considered favourable for amphoteric oxides [9]. This reaction pathway probably involves dissociative adsorption of a carboxylic acid molecule on the neighbouring Lewis acid and base sites of Zn-Cr oxide followed by non-dissociative adsorption of another acid molecule on adjacent Lewis acid site. Abstraction of α-hydrogen and C–C bond formation lead to the β-ketoacid intermediate. The latter is decarboxylated to yield ketone together with CO$_2$ and H$_2$O. The formation of C–C bond may be the rate-limiting step, as found for
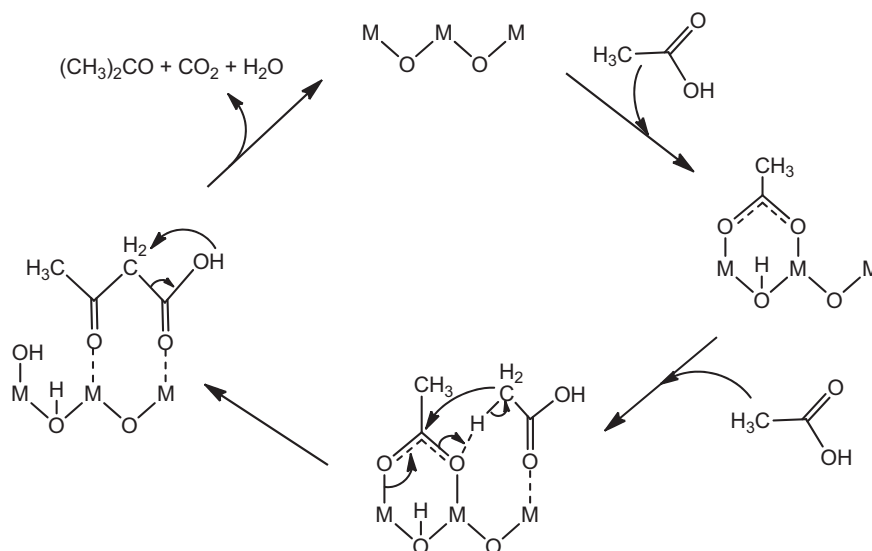
Scheme 2. Proposed mechanism for ketonisation of carboxylic acids via β-ketoacid intermediate route.
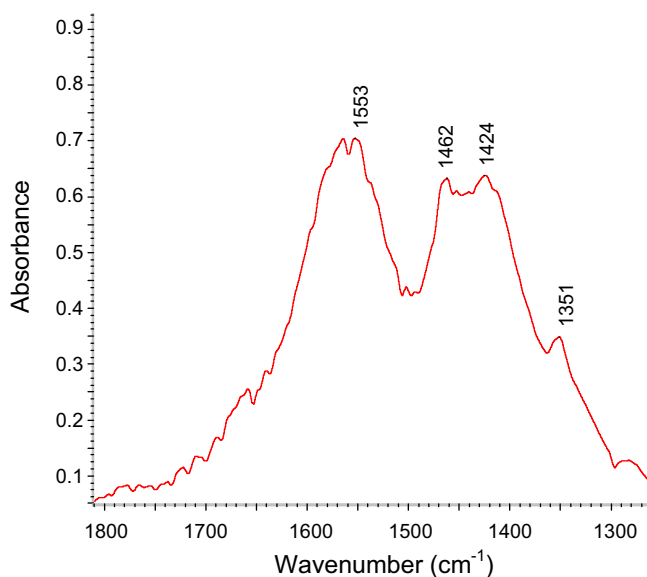

Fig. 8. DRIFT spectrum of acetic acid adsorbed on Zn-Cr (10:1) oxide after evacuation at 160 °C/10^{-5} bar for 1 h.

ketonisation of acetic, propionic and butyric acids over Ru/TiO$_2$ [30]. The higher catalytic activity of Zn-Cr oxide as compared to ZnO and Cr$_2$O$_3$ may be explained by more efficient activation of acid molecule when it bridges different metal sites.

Ketonisation over redox active CeO$_2$-Mn$_2$O$_3$ oxide has been proposed to occur via the β-ketoacid route involving a redox cycle [11]. This mechanism involves dissociative adsorption of acid molecules to form surface carboxylates, abstraction of α-hydrogen atom from surface carboxylate to form an anion radical and its addition to another carboxylate to produce β-ketoacid followed by decarboxylation to yield ketone. The surface metal in oxide may be reduced by the abstracted α-hydrogen atom and re-oxidised by the desorbed hydroxyl radical. Such redox cycle, however, is unlikely for the Zn-Cr oxide which lacks any significant redox ability.

4. Conclusions

We have demonstrated that bulk Zn-Cr mixed oxides with a Zn/Cr atomic ratio of 1:1–20:1, prepared by co-precipitation

of Zn(II) and Cr(III) hydroxides, are active and durable catalysts for the gas-phase ketonisation of carboxylic acids (acetic and propionic) at 300–400 °C and ambient pressure to form acetone and 3-pentanone, respectively. Amongst them, Zn-Cr (10:1) oxide shows the best performance. In contrast, the parent oxides ZnO and Cr$_2$O$_3$ exhibit only a poor ketonisation activity. Supporting the Zn-Cr oxide on TiO$_2$ and γ-Al$_2$O$_3$ further enhances its catalytic activity. The 20%Zn-Cr/Al$_2$O$_3$ catalyst gives 97% selectivity to 3-pentanone at 99% conversion of propionic acid at 380 °C. Zn-Cr oxides have been characterised by BET, XRD, DRIFTS of pyridine and acetic acid adsorption and microcalorimetry of ammonia adsorption. A mechanism for ketonisation of carboxylic acids via β-ketoacid intermediate route has been proposed.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.10.028.

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